Optimizing The Usage of Liquid Smoke from Coconut Shells as Natural Preservative for Fresh Fisih

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Abstract : Through these times the handling process or preservation method offresh fish caught by fishermen is done only with ice refrigeration because this method is considered to be the most effective one. However, the fuel price is rising today and make their buying power of ice cubes for preserving their commodities felt more difficult. Therefore it is necessary to seek other alternate ways to preserve fish that cheap, easy to find, with real effect in maintaining the quality of fresh fish and harmless or safe to be used for fresh fish preservation. Liquid smoke technology is one potential way that effective to help maintaining the quality of fresh fish by using coconut shells as the raw material. The purpose of this research is achieving the best result quality from time duration of drying process in coconut shells into liquid smoke.

This research is using experiment method to find the duration of drying time of coconut shells.The research started with cleansing, chopping, and drying the coconut shells for 0 day, 1 day, 2 days and 3 days.Next, the researcher employs a pyrolysis process which followed by redistillation process and columnfiltration. The resulted liquid smoke grade 3 and grade 1 then will be analyzed by GC-MSandLC-MS.Treatment of the experimental fish conducted by measuring duration of drying time of coconut shells variabel where its result then undergoes organoleptictest of colour, odor or scent, texture and taste.

The result of this research is able to find duration of optimum drying time (3 days) with water content value of 1,96%, acidity concentration value of 6,25%, and pH value of 1,9.Whereas for the amount of yield (*rendemen*) is 35,8% on 0 day.

Keywords : drying process, liquid smoke, preservation, fish.

Introduction and Experimental

The maintaining or handling process of fresh fish by refrigerating method using ice cubes is the most effective method selected by fishermen. Fish are food product that really easy to stale. Their decomposition will happen shortly after they were caught or die.In tropical weather conditions, fish will decay within 12-20 hours depends on kinds of species, fishing device/rods, or ways to capture the fish. Refrigeration or cold storage able to extends the fish's storage time.In temperature of $15\text{-}20^0$Cthey can be stored for about 2 days, in temperature of 5^0Cthey can lasts for about $5-6$ days, while in temperature of 0°C the fish can be stored until $9-14$ dayson condition of depends to its species. Fish treatment by preservation process is necessary to make this food stock still can be consumed in good/ unchange conditions in a longer time. The fish preservation method basically has a purpose to prevent decomposing bacteria entering fish bodies for creating damages in their meat. Some of the reasons of these damages are caused by high water content (80 %) in their bodies along with its pH that closely to neutral position, completed by highly nutrient contents in which will make fish as an excellent media for

bacteria and other microorganism to grow. This defective aspect of fresh fish can obstruct selling/marketing efforts from these fishery activities which in the end resulting a great loss for its sellers. Thus, it is necessary to find other ways to prolong the storage time and storability power of these fishery products during the postime of harvesting through food processing or preservation process. Many fishermen are using ice cubes to refrigerate fish in order to extend the storage time of their commodities before it gets to the consumers.

The proper antimicrobial usage can be use to prolong fish storage time and safety guarantee from this food product. Hence, it willrequire alternatives of antimicrobial material from natural source which is harmless for comsuption and able to suspend microbial growth inside the product by its primary function to slow down the food deteriation due to some microbial activities. Thus, the researcher selects another material as harmless natural antimicrobial that can be safe to consume by the usage of liquid smoke which will be applied for suspending any microbial activities. Liquid smoke is chemical substance as the end product from smoke distillation by combustion method. It contains of several chemical compounds which potentially or assume can be use as raw ingredients for preservative substances, antioxidants, disinfectants, or play acts as bio pesticides (Nurhayati, 2000). Basic material for liquid smoke in this research is coconut shells in which Indonesia considers to be one of the main plantation commodities of coconut (*Cocosnucifera*). Moreover, the increasing production of coconut commodity also creating problem of leftover materials such as coconut shells waste that continue to pile up which in the end can affect or distrub human health.

According to Girard(1992), two primary compounds in liquid smoke which identified to have bactericidal/bacterostaticeffect are phenol and some organic acids. There is a combination between functional components from phenol to organic acids which work in a cynergy to prevent and control microbes growth (Pszczola dan Astuti, 2000).Whereas in liquid smoke, it can affect the flavour, pH, and product storage time because carbonyl will react to protein and creating colours of its product and phenol which acting as primary source of flavour is showing bacteriostatic activities and antioxindants. The purpose of this reseach implementation is determining the duration of drying time in raw material for making high quality liquid smoke that can be applied for preserving fresh fish.

Research Methods

The raw material for this research is 3 kilograms of coconut shells. Fuel for the pyrolysis process is Liquid Propane Gas or LPG. Some chemical substances that applied for the analysis are SeO_2,K_2SO_4,$CuSO_4.5H_2O$,thick HCl, $NaOH2N$,H_3BO_3, NaCl,mm(methyl red indicator),pp(phenophthaliein indicator),distilled water(aquades),thickH_2SO_4,solvent hexane, alcohol,BromatBromida0,2N,KIand$Na_2S_2O_3$ 0,1N. The equipment used in this research is pyrolysis reactor made from stainless steel pipe with tar capture device and a set of condensation device. It also needed a distillation process that flowing into active zeolite filtration column then followed by fictrscarbonactive column for attaining result of liquid smoke grade 1 and 2. The research methods that will be applied in this research is laboratory experimental method. Some laboratory equipments employed for analyzing the result of liquid smoke are pH meter by *Waterproof* brand, closed (lid) Erlenmeyer, thermometer, separator bottle, titration devices, and standard glasses of Chemistry Lab. While the main devices used in this research are *Gas Chromatography and Mass Spectrometri*(GCMS) spectrometerby Hewlett Packard brand (GC 6890 MSD 5973 equipped with *Chemstation* database system) and *LiquidChromatography Mass Spectrometri* (LCMS) by Shidmadzu brand with HP5 column in 30 meter lenght.

Research Implementation

The implementation begin with coconut shells as the basic ingredient which had been cleansed from its fibres and chopped down in to smaller size are being dried then gave label of variables (0 day, 1 day, 2 days, and 3 days). Next, coconut shells are place inside pyrolysisreactor and heated with temperature of 250^0C for five hours until it produces three fractions: 1) solid fraction in a form of high quality shell charchoal, 2) heavy fraction in a form of tar, 3) light fraction in forms of smoke and methane gas. The resulted liquid smoke is not ready to be used for food preservatives because it may contains some hazardous materials, therefore it needs a further liquid smoke purification / distillation to minimize amounts of tarinside the smoke.

The liquid smoke that formed from smoke condensation in the pyrolysis process will be precipitate first for about a week before the liquid taken and put inside distillation device in the temperature around of 150^0C then the result from destillate will be collected. Next, outcome from distillates.
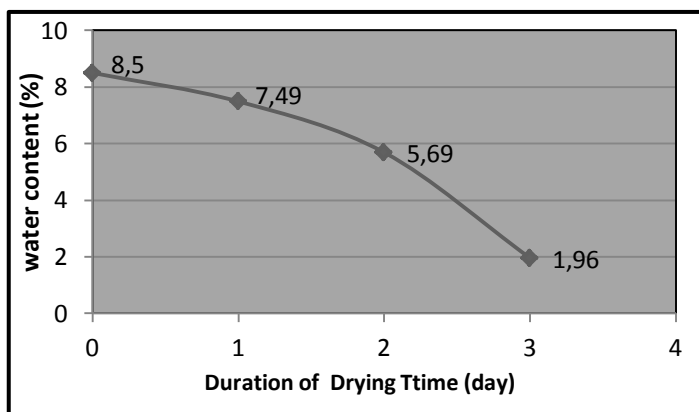
From the finding of this research,there are some parameters employ to measure the quality of liquid smoke resulted from coconut shells. Where in the beginning is finding out about duration of drying time to its water content as displays in picture 1 below :

The resulted liquid smoke then will be tested by standard method that conveys several parameters such as total phenol, acid and benzo(a) pryrene contents. Whereas for the analysis applied to ensure the quality of resulted liquid smoke in this research will be use GC/MSandLC/MS devices.which is passed on active carbon column for perfecting the end result of high quality liquid smoke as food preservatives which is safe, natural and effectivefiltration will be passed on by active zeolites and followed by further filtration process

Result and Discussions

Water Content

Water content is one important factor in determining the quality of liquid smoke that produced because the lesser water content thenat the time of pyrolysis process happen, this condition will make combustion process goes faster and yield (*rendemen)* that has low water content will produce only small portion (low) of liquid smoke because the water inside its basic ingredients reduces a lot
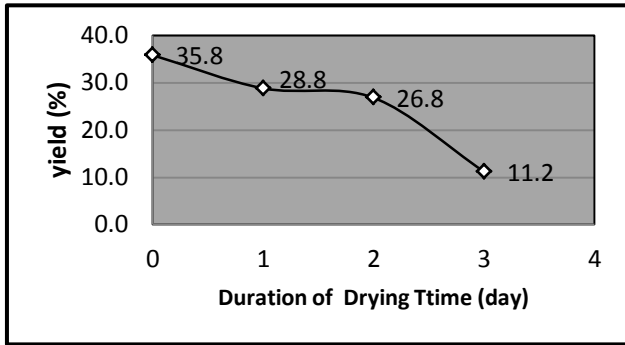

Picture 1. The relationship between water content inside coconut shells to duration of drying time of raw material.

Picture number 1 is showing a graphic curve gradually declining which tells that the longer duration of drying time to dry up the raw material before pyrolysis process happen makes the content of water inside the shells decreases for about 1,96 % due to evaporation process from ambient temperature. Thus, the longer duration of drying time will make the water content inside raw material decreases in accordance to (or depends on) duration of drying time.

A fact there exists water content inside wood (coconut shells) become closely related to hygroscopic trait from wood which posses affinity trait to water and make wood will not dried entirely. Therefore, the higher its water content, then, the bigger energy needed to evaporate the water.

Yield

Yield is also one of important parameter to find out the result of a process. Liquid smoke in this research is produced through smoke condensation process will be expelled by pyrolysisreactor. During pyrolysisprocess there will be evaporation of several kinds of chemical compounds. Data of resulted liquid smoke that produced during the pyrolysisstage are display on picture 2 below :
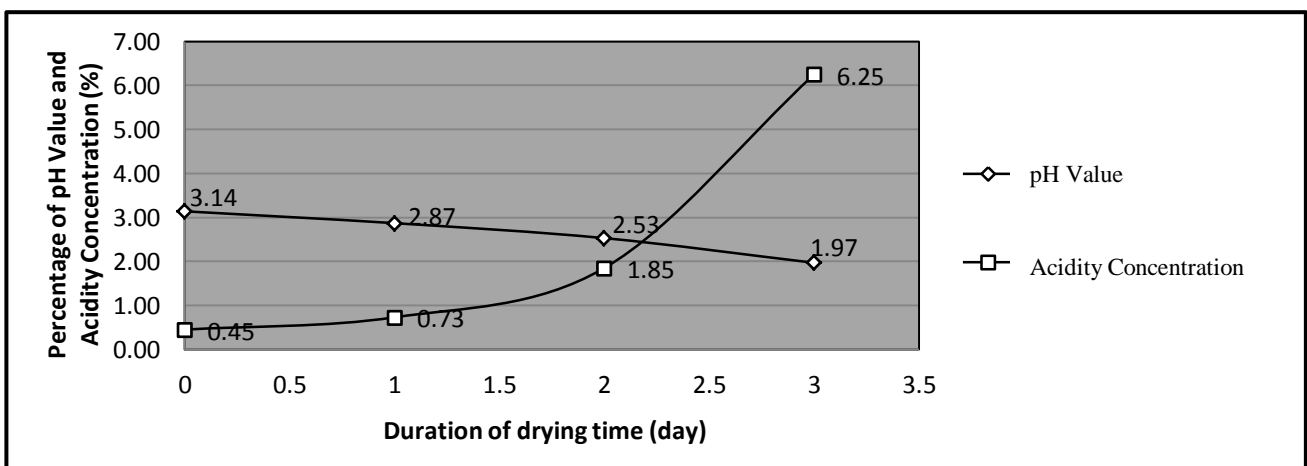
Picture 2. The relationship between yield of liquid smoketo duration of drying time of coconut shells.

The measurement result of liquid smoke yield (*rendemen)* from coconut shells is showing the highest value of liquid smoke yield (*rendemen)* is35,8% with duration of drying time of 0 day. Amount of resulted liquid smoke yield (*rendemen)* produced by pyrolysis process is highly dependent to duration of drying time of the coconut shells. With explanation of lots of water contents inside the shells will influence the amount of yield (*rendemen).* Water content inside coconut shells on 0 day duration of drying time is greater than water content on3 days duration of drying time which bring higher percentage of the resulted condensate. It happens because during the combustion process, water content inside the raw material also evaporate within temperature of 100^0C then undergoes condensation when water vapor passing through the condensor until it increasing the amount of resulted liquid smoke condensate. Differences on amount of yield (*rendemen)* from smoke distillate causedby the higher water content inside the raw materialthat makes the higher amount of resulted yield (*rendemen)* from water distillate. Meanwhile, difference on yield (*rendemen)* from liquid smoke is likely caused by the duration of drying time of raw material because they have different amount of water content inside coconut shells during the dyring process.

pH Value and Acidity Concentration

Quality of liquid smoke is highly dependent to the composition of several chemical compounds inside the smoke.The quality of resulted liquid smoke in this research will be determine by pH value and acidity concentration as these two indicators are having the greatest role as antimicrobial substance. Data research displays in picture 3 below:

Picture 3. The relationship between pH value and Acidity Concentration to Duration of drying time.

Resulted liquid smoke that produced from pyrolysis process is increasing the acidity concentration. In picture 3 is showing that the higher of its acidity concentration the lower its pH value. During 0 day duration of drying time is showing high water content because research material was not entirely dry and resulting a lower acidity concentration (0,45 %) which will bring high pH value (3,14). On the contrary, for 3 days duration of

drying time, water content value is low because during condensation process, yield (*rendemen)* outcome is getting thickeruntil it also increases the thickness of active substance inside, such as acetate acid which leads to high acidity concentration (6,25 %) and lower pH value (1,97). These figures demonstrate the resulted liquid smoke has acidic characteristic. The acid character comes from acidic compounds which contains inside the liquid smoke such as acetate acid, in particular, along with other acidic compounds. The acidic compounds resulted from liquid smoke are found in the end process of cellulose pyrolysis stage (Vivas, 2006)**.**

Higher acidity concentration from the liquid smoke will make the ability to suppress growth of microorganism from these liquid smoke also gets higher. It will be strengthen by its pH value that goes lower.This finding is in accordance to Pszczola opinion (1995) which said that there are two most important compounds that able to suppress microorganism or barctericide/barteriostatic namely as phenol and organic acid compoundbecause combination of these compounds are able to impede the growth of microbes inside the research material therefore it also be said that these two compounds have strong role as antioxidant agents. Inside the pyrolysis stage there was cellulose and hemicellulose processes which at early stage will result glucose and at second stage will result acetat acid build-ups with its homologous, together with water and small parts of furanand phenol(Girard, 1992).

It explains that the more water content inside raw material during the drying process willaffect on its acidity concentration and pH value of the resulted liquid smoke. Acid content is one of chemical trait which determines the quality of liquid smoke being produced, while organic acid that has important role in liquid smoke production is acetate acid. It is due to hemicellulose component inside coconut shells that reach 27,7 % which adequate to produce big amount of acid. Hemicellulose is wood component that if undergoes a decomposition process will creates some organic acid compounds such as acetate acid. In addition, the difference of pH value from coconut fibers and the shells also being affected by acidity concentration.

If the pH value of liquid smoke is low, then the resulted liquid smoke will have a high quality because it will entirely affecting on preservation value and storage time of smoke product or its organoleptic trait. According to Yatagai (2004) as stated by Puji Lestari (2010) a good pH value of liquid smoke is ranging between 1,5 – 3,7 because inside this low pH condition microbes that have spores can not live and proliferate thus low pH can act as blocker to suppress the growth of decomposer (microbes).

A Test For Storability of The Fresh Fish

The deterioration of fish quality that leads to decomposition process mainly caused by enzim, chemical and bacteria activities. Enzymatic activities happen by tearing down parts of fish bodies which resulted in the change of flavor, odor, appearance and texture of the fish. The chemical activities happens when there is a fatty oxidation from the fish flesh in progress because oxygen in the air will isolate fatty component from the flesh and create awful smell (*rancid)* coming from the flesh.

4a-1. 3 days of drying time

4a-2. 2 days of drying time

4a-3. 1 days of drying time

4a-3. 1 days of drying time

Picture 4a. Duration of Storage Time from 0 – 1 day

From pictures of 4a-1 to 4a- 3 with drying time from 1 day to 3 days during storage time 0-1 day has showed that fish appeared to have clear and bright eyes with fresh odor came from the gills, has brighter colours

of its body which also has fresh and more supple flesh. This expected appearance was caused by several substances inside the liquid smoke such as formaldehyd, acetaldehyd,carboxylix acid (formic acid, acetate, butyrate), phenol, cresol, primary and secondary alcohols, ketones,et cetera, that able to suppress the bacterium activities (bacteriostatic).

4b-1. 3 days of drying time　　**4b-2**. 2 days of drying time　　**4b-2**. 1 days of drying time

Picture 4b. Duration of Storage Time of 2 days

From pictures of 4b-1 to 4b-3 are showing that the skin tone of the fish remains darker although the smell was still fresh. During storage time up to 2 days, the fish remain fresh although its freshness decrease from storage day 1 and the skin felt a little dry. It means that preservation process is in progress and reducing the water content which is the factor that trigger decomposition activity because on the second day there was some remains of acidic content that still able to block the growing bacteria.

4c-1. 3 days of drying　　**4c-2**. 2 days of drying time　　**4c-2**. 1 days of drying time

Picture 4c. Duration of Storage Time of 3 days

From picture of 4c-1 is showing that fish in day 1 seen with redder eyes when compare to fish with 2 days or 3 days drying time. While for fish in 2 days drying time, it has redder eyes than 3 days drying time fish, along with changing of its body colour that gradually brighter than fish in 2 days or 1 day of drying time. In 3 days drying time the fish will have stench foul (rotten acid/ rancid) when compare to fish on 2 days or 1 day of drying time. The unpleasant odor occurs because of bacterial activity which work more active when fish begin to die. Bacteria will strike by tearing down or destruct body tissues so that the flesh composition of the fish altered. Then decomposition will take place because of fatty degradation that releaseunpleasant odor due to oxidation process or fatty hidrolisis, where both of them are occur because microbial activities inside the flesh. Fatty oxidation that happens is the primary cause which determine the quality of fish meatinside fish body tissues. Whereas for the fish with longer drying time (3 days) is showing a better result because of coconut shells liquid smoke has higher acidic compound and lower pH value than fish on 1 day or 2 days of drying time. Therefore, the storage time will be longer in fish on 3 days drying process than those in 1 day or 2 days of drying process. Coconut shell liquid smoke turns out to have longer durability until 2 days more in room temperature. More than these times, it will make fresh fish begin to experience decomposition process.

Conclusion

Liquid smoke from coconut shells which experience drying process for 3 days has longer storage time (2 days) in room temperature than fresh fish with coconut shells drying time for 2 days or 1 day.

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